Chemistry of Heterometallic Phenyl Imido and Phosphinidene Clusters

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Received November 6, 1992

Triruthenium imido cluster $\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-NPh})^{(1)}$ reacts with tungsten hydride $\text{LW}(\text{CO})_3\text{H}$ to afford heterometallic imido clusters $\text{LWRu}_2(\text{CO})_8(\mu\text{-H})(\mu_3\text{-NPh})$, $\text{L} = \text{Cp}$, (**IIa**); $\text{L} = \text{Cp}^*$, (**IIb**), whereas the respective phosphinidene complexes $\text{LWRu}_2(\text{CO})_8(\mu\text{-H})(\mu_3\text{-PPh})$, $\text{L} = \text{Cp}$, (**IXa**); $\text{L} = \text{Cp}^*$, (**IXb**), were generated via reaction of $\text{Ru}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-PPh}_2)$ with $\text{CpW}(\text{CO})_3\text{H}$ and with $\text{Cp}^*\text{W}(\text{CO})_3\text{H}$ followed by thermolysis in the presence of carbon monoxide. Their molecular structure, solution dynamics, and the subsequent reaction with hexafluoro-2-butyne are presented.

KEY WORDS: Heterometallic cluster; ruthenium; tungsten; imido; phosphinidene.

INTRODUCTION

The chemistry of transition metal clusters possessing imido [1] and phosphinidene [2] ligands has been investigated extensively in recent years. We have been interested in the synthesis of heterometallic imido clusters $\text{LWRu}_2(\text{CO})_8(\mu\text{-H})(\mu_3\text{-NPh})$, $\text{L} = \text{Cp}$, (**IIa**); $\text{L} = \text{Cp}^*$, (**IIb**), via treatment of $\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-NPh})$ with tungsten hydrides $\text{LW}(\text{CO})_3\text{H}$ [3]. The corresponding phosphinidene complexes $\text{LWRu}_2(\text{CO})_8(\mu\text{-H})(\mu_3\text{-PPh})$, $\text{L} = \text{Cp}$, (**IXa**); $\text{L} = \text{Cp}^*$, (**IXb**), were generated from phosphido complex $\text{Ru}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-PPh}_2)$ and $\text{LW}(\text{CO})_3\text{H}$ in refluxing toluene solution [4]. Here we summarize the synthesis and characterization of these heterometallic phenylimido and phosphinidene clusters. Attention

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is focused on the subsequent reactivity, such as reactions with hexafluoro-2-butyne. For the reaction of **IIa**, we isolated an alkenyl-imido complex $\text{CpWRu}_2(\text{CO})_7(\mu_3\text{-NPh})[\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)]$ (**IIIa**) in over 65% yield and a second cluster compound $\text{CpWRu}_2(\text{CO})_5(\mu\text{-NPh})[\text{C}_2(\text{CF}_3)_2][\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)]$ (**IV**) in a small quantity. The crystal structure of **IV** suggests that it is generated via sequential addition of two alkyne molecules but the reactivity indicates that its formation has not passed through the complex **IIIa** as an intermediate.

EXPERIMENTAL PROCEDURE

Infrared spectra were recorded on a Bomen M-100 FT-IR spectrometer. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AM-400 (400 MHz) instrument. Mass spectra were obtained on a JEOL-HX110 instrument operating in fast-atom bombardment (FAB) mode. All reactions were performed under a dinitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254} , E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F_{254} , E. Merck). Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

Reaction of **IIa** with Hexafluoro-2-butyne

A toluene solution (15 ml) of $\text{CpWRu}_2(\text{CO})_8(\mu_3\text{-NPh})(\mu\text{-H})^{(3)}$ (150 mg, 0.185 mmol) and excess of hexafluoro-2-butyne was placed in a 50 ml sealed tube and heated at 100°C for 10 minutes. The color of solution gradually changed from orange to dark brown. After evaporation of the solvent *in vacuo*, the residue was separated by TLC (silica gel, dichloromethane:hexane = 1:1) and recrystallization, giving 104 mg of $\text{CpWRu}_2(\text{CO})_7(\mu_3\text{-NPh})[\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)]$ (**IIIa**, 0.116 mmol, 60%) in addition to an orange-red complex $\text{CpWRu}_2(\text{CO})_5(\mu\text{-NPh})[\text{C}_2(\text{CF}_3)_2][\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)]$ (**IV**, 14 mg, 0.014 mmol, 7.6%).

Spectral data for **IV**: MS (FAB, ^{102}Ru , ^{184}W), m/z 1009(M^+). IR(CCl_4): $\nu(\text{CO})$, 2090(vs), 2057(s), 2027(m), 2020(s), 2000(w) cm^{-1} ; ^1H NMR (400 MHz, THF- d_8 , RT): δ 7.46 (t, 2H, $J_{\text{H-H}} = 7.7$ Hz), 7.25 (t, 1H, $J_{\text{H-H}} = 7.4$ Hz), 6.74 (broad, 2H), 6.29 (s, 5H), 2.95 (q, 1H, $J_{\text{F-H}} = 8.0$ Hz); ^{19}F NMR (282 MHz, THF- d_8 , RT): δ -41.77 (q, 3F, $J_{\text{F-F}} = 14.4$ Hz), -42.19 (q, 3F, $J_{\text{F-F}} = 10.2$ Hz), -49.86 (q, 3F, $J_{\text{F-F}} = 14.4$ Hz), -54.29 (m, 3F, $J_{\text{F-F}} = 10.2$ Hz, $J_{\text{F-H}} = 8.0$ Hz); ^{13}C NMR (100 MHz, THF- d_8 ,

RT): CO, δ 204.6, 196.9, 196.3, 195.6, 195.3; δ 181.1 (*q*, CCF_3 , $J_{\text{C-F}} = 35$ Hz), 170.0 ($J_{\text{W-C}} = 21$ Hz, *i*- C_6H_5), 153.7 (*q*, CCF_3 , $J_{\text{C-F}} = 40$ Hz), 146.0 (*q*, CCF_3 , $J_{\text{C-F}} = 39$ Hz), 133.7 (*q*, CF_3 , $J_{\text{C-F}} = 274$ Hz), 132.4 (*q*, CF_3 , $J_{\text{C-F}} = 276$ Hz), 131.4 (*o,m*- C_6H_5), 131.3 (*q*, CF_3 , $J_{\text{C-F}} = 276$ Hz), 130.5 (*q*, CF_3 , $J_{\text{C-F}} = 275$ Hz), 129.4 (*p*- C_6H_5), 122.0 (*m,o*- C_6H_5), 107.6 (C_5H_5), 28.1 (*q*, CHCF_3 , $J_{\text{C-F}} = 39$ Hz). Anal. Calcd. for $\text{C}_{24}\text{H}_{11}\text{F}_{12}\text{N}_1\text{O}_5\text{Ru}_2\text{W}_1$: C, 28.62; H, 1.10; N, 1.39. Found: C, 28.52; H, 1.16; N, 1.35.

Reaction of IIIa with Hexafluoro-2-butyne

A toluene solution (15 ml) of **IIIa** (20 mg, 0.116 mmol) and excess of hexafluoro-2-butyne was placed in a 50-ml sealed tube and heated at 120°C for 25 minutes. After evaporation of the solvent *in vacuo*, the residue was separated by TLC (silica gel, dichloromethane:hexane = 1:1), producing 8.5 mg of **IIIa** (0.116 mmol, 43%) and approximate 0.8 mg of **IV** (0.014 mmol, 2%).

Reaction of IXb with Hexafluoro-2-butyne

A toluene solution (10 ml) of $\text{Cp}^*\text{WRu}_2(\text{CO})_8(\mu\text{-H})(\mu_3\text{-PPh})_4$ (**IXb**, 85 mg, 0.099 mmol) and excess of hexafluoro-2-butyne was placed in a 30-ml sealed tube and heated at 100°C for 5 minutes. The color of the solution gradually changed from red to deep red. After evaporation of the solvent *in vacuo*, the residue was separated by TLC (silica gel, dichloromethane:hexane = 1:1) and recrystallization, giving 68 mg of $\text{Cp}^*\text{WRu}_2(\text{CO})_8[\mu\text{-P(Ph)C(CF}_3\text{)CH(CF}_3\text{)}]$, (**X**, 0.067 mmol, 68%) as red crystalline solid.

Spectral data for **X**: MS (FAB, ^{102}Ru , ^{184}W), m/z 1018 (M^+). IR(C_6H_{12}): $\nu(\text{CO})$, 2079(vs), 2044(vs), 2023(s), 2002(m), 1998(m), 1955(w), 1938(vw), 1867(w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , RT): δ 7.50–7.42 (*m*, 5H), 2.73 (*q*, $J_{\text{H-F}} = 9.0$ Hz), 1.84 (*s*, 15H); ^{19}F NMR (282 MHz, CDCl_3 , RT): δ -44.64 (3F, $J_{\text{F-F}} = 14.5$ Hz, $J_{\text{F-P}} = 3$ Hz), -53.16 (3F, $J_{\text{F-F}} = 14.5$ Hz, $J_{\text{F-H}} = 8.7$ Hz, $J_{\text{F-P}} = 1.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3 , RT): CO, δ 218.8 (*d*, $J_{\text{P-C}} = 12$ Hz), 215.6 (*d*, $J_{\text{P-C}} = 3.1$ Hz), 201.3, 200.5, 199.2 (2C), 194.4 (*d*, $J_{\text{P-C}} = 5$ Hz); δ : 140.3 (*d*, *i*- C_6H_5 , $J_{\text{P-C}} = 7$ Hz); ^{31}P NMR (161 MHz, CDCl_3 , RT): δ 106.5 ($J_{\text{W-P}} = 257$ Hz). Anal. Calcd. for $\text{C}_{28}\text{H}_{21}\text{O}_8\text{F}_6\text{PRu}_2\text{W}$: C, 33.09; H, 2.08. Found: C, 32.83; H, 2.02.

X-Ray Crystallography

A red-orange crystal of **IV** with dimensions $0.10 \times 0.25 \times 0.40$ mm³ was selected for X-ray analysis. The measurement was carried out on a Nonius

Table I. Experimental Data of the X-Ray Diffraction Studies for **IV**

Formula: $\text{W}_1\text{Ru}_2\text{C}_{24}\text{H}_{11}\text{F}_{12}\text{N}_1\text{O}_5$	Mol. wt. 1007.33
$a = 9.368(3) \text{ \AA}$	Triclinic, space group $P\bar{1}$
$b = 9.896(1) \text{ \AA}$	$Z = 2$
$c = 16.268(2) \text{ \AA}$	$\lambda = 0.70930 \text{ \AA}$
$\alpha = 94.90(1)^\circ$	$F(000) = 944$
$\beta = 78.81(2)^\circ$	$D_{\text{calc}} = 2.417 \text{ Mg/m}^3$
$\gamma = 110.68(2)^\circ$	$2\theta(\text{max}) = 45^\circ$
$V = 1384.0(5) \text{ \AA}^3$	$\mu = 5.41 \text{ mm}^{-1}$
Index ranges	$-10 \leq h \leq 9, 0 \leq k \leq 10, -17 \leq l \leq 17$
Transmission factors	0.526/1.000
No. of unique data, total with $I > 2\sigma(I)$	3608, 3284
No. of atoms and parameters refined	56, 407
Weighting scheme = counting-statistics	$R_F, R_W = 0.018, 0.016$
GOF = 1.82	Max. Δ/σ ratio = 0.032
Residue electron density (min/max)	
$= -0.57/0.61 \text{ e/\AA}^3$	

CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. Cell parameters were obtained from 25 reflections with 2θ angle in the range $20.22\text{--}23.08$ degrees. The 3284 unique reflections with $I > 2.0 \sigma(I)$ were corrected for absorption, Lorentz and polarization effects. Scattering factors were taken from the International Tables for X-ray crystallography (1974). All data deduction and structural refinement were performed using the NRCC-SDP-VAX packages. The structures were solved by the direct method and refined by least-squares recycle. All the non-hydrogen atoms were refined with anisotropic temperature factors. The positions of all hydrogen atoms were calculated by assuming idealized geometries; their contributions were added to the structural factor calculations, but their positions were not refined. The data collection, refinement parameters, and results of analyses are given in Table I, whereas the atomic positional parameters are given in Table II.

RESULTS AND DISCUSSION

Synthesis of WRu_2 Imido Clusters

Treatment of the triruthenium imido complex $\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-NPh})$ (**I**) [5] with tungsten hydrides $\text{LW}(\text{CO})_3\text{H}$ in refluxing toluene (110°C , 20 min) produced imido clusters, $\text{LWRu}_2(\text{CO})_8(\mu\text{-H})(\mu_3\text{-NPh})$ (**IIa**, $\text{L} = \text{Cp}$, 56%; **IIb**, $\text{L} = \text{Cp}^*$, 51%) in addition to trace proportions of $\text{Ru}_3(\text{CO})_{12}$ (Scheme 1) [3]. In complexes **IIa** and **IIb** the imido ligand

Table II. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for IV

	x	y	z	Biso
W	0.863028(23)	0.190396(22)	0.326441(12)	2.169(9)
Ru1	1.14336(4)	0.39132(4)	0.273763(23)	2.327(18)
Ru2	0.99475(5)	0.26096(4)	0.143464(23)	2.437(20)
N	0.8085(4)	0.1065(4)	0.22979(21)	2.25(19)
C1	1.3279(6)	0.3839(5)	0.2011(3)	3.6(3)
C2	1.2563(6)	0.5880(5)	0.3048(3)	3.5(3)
C3	1.1561(6)	0.3834(6)	0.0693(3)	3.8(3)
C4	0.8516(6)	0.2434(5)	0.0698(3)	3.6(3)
C5	1.0666(6)	0.1000(6)	0.0973(3)	3.6(3)
C6	1.1386(6)	0.0663(5)	0.3028(3)	3.5(3)
C7	1.0872(5)	0.1920(5)	0.3320(3)	2.53(25)
C8	1.1653(5)	0.3033(5)	0.3859(3)	3.0(3)
C9	1.3208(6)	0.3309(6)	0.4071(3)	3.8(3)
C10	0.9807(6)	0.5746(5)	0.1783(3)	3.8(3)
C11	0.9710(5)	0.4373(5)	0.2168(3)	2.53(24)
C12	0.9110(5)	0.4072(5)	0.3034(3)	2.34(23)
C13	0.8749(6)	0.5166(6)	0.3662(3)	3.8(3)
C14	0.6965(5)	−0.0082(5)	0.1920(3)	2.59(25)
C15	0.5698(5)	0.0155(5)	0.1718(3)	3.4(3)
C16	0.4674(6)	−0.0921(6)	0.1316(4)	4.6(3)
C17	0.4897(6)	−0.2206(6)	0.1106(3)	4.9(3)
C18	0.6135(6)	−0.2461(6)	0.1328(3)	4.5(3)
C19	0.7172(5)	−0.1393(5)	0.1734(3)	3.4(3)
C20	0.6596(6)	0.1966(6)	0.4366(3)	3.9(3)
C21	0.5999(6)	0.0729(6)	0.3893(3)	4.1(3)
C22	0.6802(6)	−0.0211(6)	0.3941(3)	4.1(3)
C23	0.7907(6)	0.0477(6)	0.4452(3)	4.4(3)
C24	0.7769(6)	0.1806(6)	0.4723(3)	4.1(3)
O1	1.4364(4)	0.3791(4)	0.15788(24)	5.78(25)
O2	1.3249(4)	0.7006(4)	0.32622(24)	5.54(22)
O3	1.2572(4)	0.4545(4)	0.02229(21)	5.47(22)
O4	0.7693(4)	0.2397(4)	0.02628(22)	5.68(24)
O5	1.1124(5)	0.0125(4)	0.06939(24)	6.4(3)
F1	1.0326(4)	−0.0394(3)	0.26751(21)	5.55(20)
F2	1.2670(4)	0.0943(4)	0.24526(22)	6.48(21)
F3	1.1635(4)	0.0056(4)	0.36566(20)	6.86(24)
F4	1.3147(4)	0.2528(4)	0.47107(20)	6.43(21)
F5	1.4220(3)	0.3019(4)	0.34445(19)	5.72(21)
F6	1.3879(3)	0.4688(3)	0.42986(19)	5.36(18)
F7	1.1016(4)	0.6902(3)	0.18960(21)	5.83(20)
F8	0.8542(4)	0.6098(3)	0.20634(21)	6.01(20)
F9	0.9878(4)	0.5620(3)	0.09485(19)	6.43(23)
F10	0.9678(3)	0.6545(3)	0.35285(19)	5.01(18)
F11	0.7289(3)	0.5151(3)	0.37200(19)	4.86(18)
F12	0.8861(3)	0.4908(3)	0.44467(17)	4.73(18)

adopts a triply bridging mode and the hydride is associated with the unique Ru–Ru edge. The mechanism is best understood as a metal-exchange reaction [6], in which the reactions proceed by the replacement of $\text{Ru}(\text{CO})_4$ unit by an isoelectronic $\text{LW}(\text{CO})_2\text{H}$ fragment; the co-product $\text{Ru}_3(\text{CO})_{12}$ is generated by the trimerization of the departing $\text{Ru}(\text{CO})_4$ unit. In conformity with this reaction mechanism, Geoffroy *et al.* have reported the preparation of the heteronuclear cluster compound $\text{HCoRu}_2(\text{CO})_9(\mu_3\text{-NPh})$ via addition of cobalt carbonyl anion $[\text{Co}(\text{CO})_4]^-$ to **I**, followed by protonation with HBF_4 [7].

Reactions of Imido Clusters with Hexafluoro-2-butyne

In contrast to the reactions between the parent phenylimido cluster **I** and disubstituted alkynes which yield the metallapyrrolinone complexes, the corresponding alkyne addition reactions with clusters **IIa** and **IIb** suffer from sample decomposition. However, the respective reactions with the electron-withdrawing alkyne are different: treatment of the imido cluster **IIa** with an excess of hexafluoro-2-butyne in a sealed-tube (100°C , 10 min) afforded a dark-green insertion product $\text{CpWRu}_2(\text{CO})_7(\mu_3\text{-NPh})$ ($\text{CF}_3\text{CCHCF}_3$) (**IIIa**) in 60% yield and an orange-red, double addition product $\text{CpWRu}_2(\text{CO})_5(\mu\text{-NPh})[\text{C}_2(\text{CF}_3)_2][\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)]$ (**IV**) in 8% yield, whereas the respective reaction with the Cp^* derivative **IIb** gave the alkenyl cluster (**IIIb**) in nearly 90% yield (Scheme 1) [8]. No double-addition product was observed for the reaction with Cp^* derivative **IIb**.

Scheme 1

Characterization of **III** and Structural Determination of **IV**

Complexes **IIIa** and **IIIb** possess an isosceles WRu_2 cluster core, a face-bridging imido ligand and an edge-bridging *cis*-alkenyl ligand. The

Fig. 1. Molecular structure of **IV**. Bond lengths (Å): W–Ru(1) = 2.7047(10), W–Ru(2) = 3.0319(7), Ru(1)–Ru(2) = 2.7395(8), W–N = 1.792(4), Ru(2)–N = 2.211(3), W–C(7) = 2.114(4), Ru(1)–C(7) = 2.111(4), C(7)–C(8) = 1.424(7), Ru(1)–C(8) = 2.161(4), W–C(12) = 2.082(4), Ru(2)–C(11) = 2.082(5), Ru(1)–C(11) = 2.201(4), Ru(1)–C(12) = 2.195(4), C(11)–C(12) = 1.426(6).

mode of the imido ligand is analogous to the homometallic analogues $\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-NPh})$, $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-NPh})$ and $\text{Ru}_3(\text{CO})_8(\text{DPPM})(\mu_3\text{-NPh})$ [9], whereas the alkenyl ligand resembles that of the regular edge-bridging alkenyl ligand observed in several group 8 dinuclear [10] and trinuclear alkenyl complexes [11].

For complex **IV**, a single-crystal X-ray diffraction study has been carried out. A view of the molecular structure is presented in Fig. 1 along with the selected parameters of bond lengths and angles. The cluster core consists of an isosceles W_2Ru arrangement with W–Ru(1) = 2.7047(10), Ru(1)–Ru(2) = 2.7395(8), and W–Ru(2) = 3.0319(7) Å. The imido ligand bridges the W–Ru(2) edge with W–N = 1.792(4) and Ru(2)–N = 2.211(3) Å, while the *cis*-C(CF₃)=CH(CF₃) group lies on the W–Ru(1) edge and the hexafluoro-2-butyne fragment adopts the typical $\mu_3\text{-}\eta^2$ -mode [12]. Although complex **IV** might be considered a derivative of **IIIa**, generated via addition of one additional hexafluoro-2-butyne and elimination of two CO molecules, this hypothesis is excluded because the direct reaction of **IIIa** with diphenylacetylene yields no stable cluster molecule

and with hexafluoro-2-butyne affords only trace **IV** ($\leq 2\%$) under identical conditions. Thus, the formation of **IV** does not involve complex **IIIa** as intermediate but proceeds via the simultaneous addition of two hexafluoro-2-butyne molecules to imido cluster **IIa**, in which one hexafluoro-2-butyne fragment remains the same but the second one couples with the bridging hydride to give the observed alkenyl fragment. No attempt was made to verify the proposed mechanism.

Scheme 2

Alkenyl Rearrangement on the WRu_2 Metal Triangle

Complex **IIIa** underwent an unprecedented imido-ligand-assisted alkenyl migration. Thermolysis of **IIIa** under CO in toluene (1 atm, 110°C , 1.5 hour) afforded two isomeric derivatives **Va** (amber, 40%) and **VIa** (orange, 36%) in addition to some unreacted precursor (15%). Extending the reaction period to 4 hr, we isolated **VIa** as major cluster product in approximate 82% yield. This result indicates that isomer **Va** is best considered an intermediate in the alkenyl rearrangement and that the isomers **IIIa** and **VIa** are the kinetic and the thermodynamic products, respectively (Scheme 2) [8]. X-ray structural analysis of **Va** indicates that this molecule possesses an edge-bridging $\text{W}=\text{N}(\text{Ph})\rightarrow\text{Ru}$ imido ligand and a face-bridging alkenyl groups. The derivative **VIa** is related to its precursor **IIIa**, possessing a face-bridging imido ligand and an edge-bridging alkenyl ligand associated with a $\text{W}-\text{Ru}$ edge instead of a $\text{Ru}-\text{Ru}$ edge. Consistent with this assignment the ^{13}C NMR spectrum of **VIa** shows one $\text{W}-\text{CO}$ signal at δ 230.6 ($J_{\text{W}-\text{C}}=160$ Hz) and six $\text{Ru}-\text{CO}$ signals in the range δ 199.2–186.1. The structure of its phosphine derivative, generated via simple substitution and *ortho*-metallation, lends strong support to this postulate [8]. Based on the structural studies of **IIIa**, **Va**, and **VIa** and the chemical reactions, it is obvious that the *cis*-alkenyl group undergoes migration from the unique $\text{Ru}-\text{Ru}$ edge to a $\text{Ru}-\text{W}$ edge through the face-bridging alkenyl fragment. The imido ligand moves simultaneously from face-bridging to edge-bridging and finally back to the face-bridging position to balance the electron distribution. This ligand movement differs greatly from the typical

$\sigma \rightarrow \pi$, $\pi \rightarrow \sigma$ rearrangement (vinyl group flipping) observed for the edge-bridging alkenyl ligand [13].

Furthermore, the application of a CO atmosphere is essential to prevent unwanted cluster degradation, because if the reaction is carried out under nitrogen we observed substantial sample decomposition within 20 minutes. In contrast to **IIIa**, the respective Cp* derivative **IIIb** is essentially inert under CO atmosphere but reacts by elimination of one CO molecule to afford a hydrido-alkyne complex $\text{Cp}^*\text{WRu}_2(\text{CO})_6\text{H}(\mu\text{-NPh})[\text{C}_2(\text{CF}_3)_2]$ (**VIIb**) under nitrogen atmosphere (Scheme 3). This process is irreversible as complex **VIIb** failed to regenerate **IIIb** upon treatment with CO but afforded a different alkenyl derivative $\text{Cp}^*\text{WRu}_2(\text{CO})_7(\mu\text{-NPh})(\text{CCF}_3\text{CHCF}_3)$ (**Vb**) in 51 % yield. The latter reaction is reversible since thermolysis of **Vb** in the absence of CO regenerated **VIIb** in 56 % yield. In general, these reactions complement those of the analogous Cp derivatives since thermolysis of **IIIa** failed to afford **VIIa** and thermolysis of **Vb** under CO gave no indication of formation of the hypothetical **VIIb**. The divergence in reactivity is probably due to the electron-releasing property of the Cp* ligand [14]. Since the Cp* ligand is a better electron-releasing group than Cp, its presence can further stabilize the W = N interaction in **Vb** and **VIIb**, and therefore retards the regeneration of the μ_3 -imido mode and prohibits the formation of **VIIb**. In **VIIb**, there is a signal at $\delta -5.83$ ($J_{\text{W-H}} = 122$ Hz) in the ^1H NMR spectra and the ^{13}C NMR spectrum shows a peak at $\delta 163.2$ with $J_{\text{C-W}} = 21$ Hz due to the *ipso*-carbon of phenylimido group, suggesting the existence of a W-bound terminal hydride and an edge-bridging imido group. These features were confirmed by single-crystal X-ray diffraction analysis.

Scheme 3

Synthesis of WRu_2 Phosphinidene Clusters

The synthesis of the WRu_2 phosphinidene complexes is less straightforward because the phosphinidene analogue of **I** has yet been synthesized. However, we circumvented this difficulty by using diphenylphosphido clusters as precursors, as many phosphinidene cluster

complexes were generated from the reaction with diphenylphosphine [15] and thermolysis of diphenylphosphido cluster via elimination of a benzene molecule [16]. In one paper, Carty and co-workers described preparation of the heterometallic cluster $\text{Cp}_2\text{Ni}_2\text{Ru}_3(\text{CO})_9(\mu_5\text{-PPh})$ [17] via condensation of $\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-PPh}_2)$ with $[\text{CpNi}(\text{CO})]_2$. Their discovery provides a hint that heterometallic phosphinidene clusters can be prepared from phosphido clusters as well [18]. Thus, we examined the reaction of the related $\text{Ru}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-PPh}_2)$ with tungsten hydride $\text{LW}(\text{CO})_3\text{H}$ because the former is known to undergo CO elimination to afford unsaturated $\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-PPh}_2)$ [19].

Scheme 4

Treatment of the triruthenium phosphido complex $\text{Ru}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-PPh}_2)$ with excess of $\text{Cp}^*\text{W}(\text{CO})_3\text{H}$ in refluxing toluene (20 min) produced a tetranuclear phosphinidene complex $\text{Cp}^*\text{WRu}_3(\text{CO})_{10}(\mu_3\text{-H})(\mu_3\text{-PPh})$ (**VIIIa**) in 45% yield (Scheme 4). The basic structure is considered a WRu_3P trigonal-bipyramidal arrangement or a distorted WRu_3 tetrahedron capped by a phosphinidene ligand; two bridging CO ligands share a common Ru vertex and a face-bridging hydride ligand is located on a WRu_2 face. Upon reaction with CO, this complex undergoes cluster degradation to afford a trinuclear phosphinidene complex, $\text{Cp}^*\text{WRu}_2(\text{CO})_8(\mu\text{-H})(\mu_3\text{-PPh})$ (**IXb**) in 72% yield. The related trinuclear Cp derivative **IXa** was prepared directly from the combination of $\text{Ru}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-PPh}_2)$ with $\text{CpW}(\text{CO})_3\text{H}$ (Scheme 4). No tetranuclear intermediate **VIIIa** was observed for this Cp derivative. The X-ray analysis indicated that the complexes **IXa** and **IXb** differ from each other by varying location of the bridging hydride ligand.

Solution Fluxionality of **IXb**

Derivative **IXa** is isostructural with the related phenylimido clusters **II** and displays a hydride peak at $\delta -17.96$ ($J_{\text{P-H}} = 15.6$ Hz) and three Ru–CO signals at $\delta 197.0$ ($J_{\text{P-C}} = 43$ Hz), 194.6 and 188.2 in a ratio 2:2:2.

In contrast, the ^1H NMR spectrum of **IXb** at 188 K exhibits two sets of signals at -19.05 ($J_{\text{W-H}} = 57.6$ Hz and $J_{\text{P-H}} = 17.6$ Hz) and -19.17 ($J_{\text{P-H}} = 14.4$ Hz) and two ^{31}P NMR signals at δ 287.0 ($J_{\text{W-P}} = 195$ Hz) and 257.6 ($J_{\text{W-P}} = 183$ Hz) in an intensity ratio 1:2.3, respectively. Based on these NMR data and the results of X-ray analyses, we propose that the dynamic behavior of **IXb** is due to rapid and reversible hydride movement from the Ru–Ru edge to the adjacent W–Ru edge. Such hydride migration is not a remarkable process because there are many precedents for the transition metal hydride complexes [20]. However, the most unusual feature is the observation of site preference of the bridging hydride. We attribute this to the enhanced electron-donating ability of the Cp^* ligand which causes an enhancement of negative charge on the tungsten atom; this charge in turn attracts the positive hydride ligand. A similar explanation has been invoked to account for the conformational preference of the $\text{LM}(\text{CO})_2$ center, $\text{M} = \text{W}$ and Mo , and the formation of semi-bridging CO ligands in the MCo_2 alkylidyne clusters [21]. In the tetranuclear clusters $\text{LWOs}_3(\text{CO})_{12}(\mu\text{-H})$ and $\text{LWOs}_3(\text{CO})_{11}(\mu\text{-H})_3$, we also noted that the hydrides have a greater tendency to connect to the W atom [22] as the auxillary ligand being altered from Cp to the electron-donating Cp^* ligand.

Scheme 5

Reactions of **IXb** with Hexafluoro-2-butyne

From the study of structure and solution dynamics of phosphinidene clusters we noticed the existence of some discrepancy between the phenylimido and phosphinidene clusters. In order to compare further their reactivity, we carried out the reactions of phosphinidene clusters **IX** with hexafluoro-2-butyne. Our result indicates that the alkyne not only reacts with hydride to afford an alkenyl fragment, but the resulting alkenyl fragment further couples with phosphinidene ligand to afford vinyl-phosphido cluster compound $\text{Cp}^*\text{WRu}_2(\text{CO})_8([\mu\text{-P}(\text{Ph})\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)])$ (**X**) (Scheme 5). This pattern is compatible with other phosphinidene clusters since the tetraruthenium phosphidene cluster $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-PPh})$ is known to react with alkyne via the formation of P–C bond, affording a

nido-cluster skeleton [23]. Some chemistry of **X** has been developed: thermolysis in toluene solution under nitrogen fails to produce a stable complex via CO elimination. However, while complex **X** was treated with triphenylphosphine we obtained a substitution product via simple replacement of a Ru bound CO ligand (Scheme 5). Heating of this phosphine derivative in toluene eliminated two CO molecules and induced the P–C bond cleavage to regenerate the μ_3 -phosphinidene ligand and the W=Ru double bond. Apparently, the good σ -donating and poor π -accepting property of the triphenylphosphine ligand has a dramatic impact on the stability and reactivity of **X**.

SUPPLEMENTARY MATERIAL AVAILABLE

A complete listing of thermal parameters, tables of nonessential bond distances and angles, hydrogen atom coordinates, and listings of the observed and calculated structural factors for complex **IV** are available from one author (Y.C.).

ACKNOWLEDGMENT

This research was supported by the National Science Council of the Republic of China (Grant No. NSC 82-0208-M007-079).

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